Rh–Rh–P isomer for the $P(C_6H_{11})_3$ derivative. The $PBu^n{}_3$ derivative consists of predominantly the linear Rh–Rh–P isomer, but there are significant quantities of the bent isomer present. The ^{19}F NMR spectra (Table I) show only one signal for the linear isomer but two for the bent isomer. In the ^1H and ^{13}C NMR spectra the linear isomers show only one type of formamidinate ligand, with inequivalent *p*-tolyl groups, but the equatorial adduct shows that both the formamidinate ligands are inequivalent. The ends of the formamidinate ligands are also inequivalent, giving rise to four sets of signals due to *p*-tolyl groups (Table II). Furthermore, the IR spectra show, beside the bands associated with the formamidinate fragments, one strong band in the range 1660–1630 cm^{-1} easily attributed to ν_{asym}(O–C–O). In each case no stretching frequencies due to monodentate trifluoroacetate groups are present. Although the spectral data do not allow an unambiguous assignment of the structure of the equatorial adducts, we nevertheless suggest structure IIa for the bent isomer, since (a) structure IIb is more sterically congested than IIa and (b) it would involve breaking of the $\overline{\text{Rh–N–C–N–Rh}}$ fragment, which has been shown to be very stable while the trifluoroacetate group is known as a good leaving group. The isomerization reported here is quite uncommon for this class of compounds, but there is some precedence for these transformations. In fact, although not directly observed, such isomerism must be operating when the axial phosphine derivatives $Rh_2(O_2CCH_3)_4L_2$ ($L = PPh_3$,[11] P(*o*-$ClC_6H_4)Ph_2$[7b]) undergo thermal ortho-metalation reactions leading to complexes where the ortho-metalated phosphine acts as a bridging ligand. Furthermore, the complex $Mo_2(O_2CCF_3)_4$ reacts with $PMePh_2$, giving class I[3b] at room temperature or class II[12] adducts under more strenuous experimental conditions.

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Registry No. $Rh_2(form)_2(O_2CCF_3)_2(OH_2)_2$, 105164-41-8; $Rh_2(form)_2(O_2CCF_3)_2(PPh_3)$ (axial isomer), 121288-94-6; $Rh_2(form)_2(O_2CCF_3)_2(PPh_3)$ (equatorial isomer), 121289-06-3; $Rh_2(form)_2(O_2CCF_3)_2(P(C_6H_{11})_3)$ (axial isomer), 121288-95-7; $Rh_2(form)_2(O_2CCF_3)_2(P(C_6H_{11})_3)$ (equatorial isomer), 121288-96-8; $Rh_2(form)_2(O_2CCF_3)_2(P(Bu^n)_3)$ (axial isomer), 121288-97-9; $Rh_2(form)_2(O_2CCF_3)_2(P(Bu^n)_3)$ (equatorial isomer), 121288-98-0; $Rh_2(form)_2(O_2CCF_3)_2(PMePh_2)$ (axial isomer), 121288-99-1; $Rh_2(form)_2(O_2CCF_3)_2(PMePh_2)$ (equatorial isomer), 121289-00-7; $Rh_2(form)_2(O_2CCF_3)_2(PPh_2H)$, 121289-01-8; $Rh_2(form)_2(O_2CCF_3)_2(PMe_2Ph)$ (axial isomer), 121289-02-9; $Rh_2(form)_2(O_2CCF_3)_2(PMe_2Ph)$ (equatorial isomer), 121289-03-0; $Rh_2(form)_2(O_2CCF_3)_2(P(OMe)_3)$, 121289-04-1; $Rh_2(form)_2(O_2CCF_3)_2(PMe_3)$, 121289-05-2; $Rh_2(form)_2(O_2CCF_3)_2(P(Bu^t)_3)$, 121289-07-4; Rh, 7440-16-6.

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Isolation and Identification of a *trans*-Bis(bipyridine) Complex of Rhodium(III). Crystal Structure of [*trans*-$Rh(bpy)_2(Cl)]_2(H_5O_3)(ClO_4)_3$: Evidence for a H_5O_3 Bridging Group

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The trans configuration of complexes of the type $M(bpy)_2XY^{n+}$ (bpy = 2,2′-bipyridine) has long been considered as rather improbable due to the steric hindrance caused by the α-protons in such structures.[1] In the case of bis(bipyridine) complexes of d^8 metal ions (Pd(II), Pt(II)), the steric strain is relieved by structural modifications.[2] In light of these trends it is quite understandable that thermal and photochemical aquation reactions of *cis*-$Rh(bpy)_2Cl_2^+$ were reported to proceed stereoretentively.[3] However, our high-pressure mechanistic studies of the photoaquation of this complex first[4] revealed some indirect and later[5] direct evidence for the formation of *trans*-$Rh(bpy)_2Cl_2^+$ and *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$. It follows that bis(bipyridine) complexes of Rh(III) can exhibit a similar cis–trans isomerization as found for related Ru(II) complexes before.[6] The configurational differences in the case of the title compound show up very well in the RhN_4XY^{n+} skeletal vibrations as they do in other cases with amine ligands. This is also demonstrated here for *cis*- and *trans*-$Rh(bpy)_2XY^{n+}$ (X, Y = H_2O or Cl$^-$). In the meantime we have succeeded in growing crystals of *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ (as the perchlorate salt) suitable for a structure determination. The results reported here not only underline the validity of our earlier conclusions but also reveal a fascinating $H_5O_3^-$ bridging group linking two $Rh(bpy)_2Cl^{2+}$ units in the solid state.

Table I. Crystal Data and Data Collection Parameters for $[Cl(bpy)_2Rh–H_5O_3–Rh(bpy)_2Cl](ClO_4)_3$

formula	$Rh_2C_{40}H_{37}N_8Cl_5O_{15}$	space group	$P\bar{1}$ (No. 2)
fw	1252.85	μ(Mo Kα), cm^{-1}	10.7
cell params		D_{calcd}, g cm^{-3}	1.81
a, Å	12.861 (2)	D_{obsd}, g cm^{-3}	1.80
b, Å	13.069 (1)	*T*, °C	25
c, Å	16.046 (5)	radiation	Mo Kα (0.7107 Å, graphite monochromator)
α, deg	63.58 (2)		
β, deg	73.80 (2)		
γ, deg	73.15 (1)	$R(F_o)$	0.043
V, Å^3	2293.05	$R_w(F_o)$	0.046
Z	2		

Experimental Section

The cis and trans complexes discussed in this paper were prepared and characterized as described elsewhere.[5] Crystals of *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ suitable for X-ray analysis were grown from a neutral aqueous solution of this complex. The light yellow compound, which may be formulated as $[Cl(bpy)_2Rh–H_5O_3–Rh(bpy)_2Cl](ClO_4)_3$, crystallizes in the triclinic space group $P\bar{1}$ or *P1*. Statistical analysis of the intensities led to the former centrosymmetric space group, and the subsequent successful solution and refinement of the structure confirmed this choice. The crystal and refinement data are given in Table I. The X-ray crystallographic data were obtained on a Enraf-Nonius CAD 4F diffractometer using graphite-monochromated Mo Kα radiation. No decomposition of the crystal was detected during the data collection. The data were corrected for Lorentz–polarization and absorption effects.

The structure was solved by means of Patterson and Fourier methods. All the calculations were done on a Univac 1100 computer using the X-ray 72 system of programs. The final *R* value was 0.043, with use of anisotropic thermal parameters for all the non-hydrogen atoms. The atomic coordinates are given in Table II.

Infrared spectra were recorded on a Nicolet 5 SX FT-IR instrument (4000–400 cm^{-1}, KBr disk) and on a Perkin-Elmer 325 grating spectrophotometer (400–200 cm^{-1}, CsI disk).

Results and Discussion

Crystal Structure. The crystal is composed of discrete $Cl(bpy)_2Rh–H_5O_3–Rh(bpy)_2Cl^{3+}$ cations and ClO_4^- anions. The most important bond lengths and angles are given in Table III. Figure 1 shows the numbering system of the atoms in the Rh(III) complex. There are two crystallographically independent *trans*-$Rh(bpy)_2Cl^{2+}$ units linked by a $H_5O_3^-$ bridge to form the trans dimer. The 3+ charge of the dimeric unit is balanced by three perchlorate ions in the crystal. The bond distances and angles

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Table II. Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Rh1	1681.8 (3)	2523.7 (4)	3294.5 (3)	Rh2	2853.8 (3)	−2504.2 (3)	1753.9 (3)
Cl1	1435 (1)	3879 (1)	3907 (1)	Cl2	3394 (1)	−3947 (1)	1210 (1)
O1	1861 (4)	1309 (3)	2772 (3)	O2	2354 (3)	−1231 (3)	2266 (3)
N11	3215 (4)	2905 (4)	2579 (3)	N21	1281 (4)	−2864 (4)	2262 (3)
C111	4072 (5)	2740 (5)	2970 (5)	C211	529 (5)	−2706 (5)	1773 (4)
C112	5115 (6)	2913 (6)	2403 (6)	C212	−570 (5)	−2776 (6)	2205 (5)
C113	5259 (6)	3254 (6)	1432 (6)	C213	−883 (6)	−2997 (6)	3161 (6)
C114	4353 (5)	3504 (5)	1018 (5)	C214	−100 (5)	−3233 (6)	3688 (5)
C115	3328 (5)	3358 (5)	1629 (4)	C215	991 (5)	−3197 (5)	3222 (4)
N12	1398 (4)	3782 (4)	2024 (3)	N22	2909 (4)	−3656 (4)	3107 (3)
C121	449 (5)	4482 (5)	1844 (5)	C221	3819 (6)	−4305 (5)	3427 (5)
C122	350 (6)	5255 (6)	912 (5)	C222	3765 (7)	−4921 (6)	4401 (5)
C123	1226 (7)	5286 (6)	177 (5)	C223	2797 (7)	−4848 (6)	5034 (5)
C124	2231 (6)	4586 (6)	363 (4)	C224	1838 (6)	−4232 (5)	4682 (4)
C125	2287 (5)	3880 (5)	1303 (4)	C225	1918 (5)	−3661 (5)	3706 (4)
N13	143 (4)	2120 (4)	4032 (3)	N23	4402 (4)	−2105 (4)	1299 (3)
C131	−778 (5)	2463 (5)	3671 (5)	C231	5091 (5)	−2299 (5)	1868 (5)
C132	−1806 (6)	2270 (6)	4269 (6)	C232	6178 (5)	−2091 (6)	1482 (5)
C133	−1870 (6)	1673 (6)	5236 (6)	C233	6542 (5)	−1699 (6)	520 (6)
C134	−920 (6)	1256 (6)	5605 (5)	C234	5813 (5)	−1440 (6)	−79 (5)
C135	88 (5)	1485 (5)	4974 (4)	C235	4740 (5)	−1637 (5)	344 (4)
N14	2017 (4)	1225 (4)	4547 (3)	N24	2834 (4)	−1358 (4)	377 (3)
C141	3017 (5)	638 (5)	4697 (5)	C241	1945 (5)	−831 (5)	−19 (4)
C142	3170 (7)	−153 (6)	5610 (5)	C242	2054 (6)	−245 (6)	−999 (5)
C143	2284 (7)	−329 (7)	6355 (5)	C243	3083 (7)	−208 (6)	−1568 (5)
C144	1236 (7)	240 (6)	6194 (5)	C244	4010 (6)	−698 (6)	−1164 (4)
C145	1136 (5)	993 (5)	5264 (4)	C245	3855 (5)	−1244 (5)	−183 (4)
O3	3509 (3)	−68 (4)	2453 (3)	Cl4	5372 (1)	8150 (2)	4140 (1)
Cl3	282 (1)	1416 (2)	1097 (1)	O41	5263 (6)	7930 (6)	5089 (4)
O31	411 (5)	198 (5)	1652 (4)	O42	6449 (5)	7840 (6)	3739 (6)
O32	1143 (8)	1889 (9)	1111 (5)	O43	5074 (5)	9361 (5)	3612 (4)
O33	337 (6)	1624 (6)	152 (4)	O44	4657 (6)	7535 (6)	4073 (5)
O34	−708 (7)	1878 (6)	1496 (6)	O52	6304 (5)	5406 (5)	1658 (4)
Cl5	7039 (2)	4814 (2)	2309 (1)	O53	7803 (6)	5485 (8)	2152 (9)
O51	6387 (6)	4547 (8)	3231 (5)	O54	7588 (5)	3777 (5)	2204 (5)

[a] The first digit in the atom numbering refers to the rhodium atom and the second to the number of the pyridine ring (see also numbering scheme in Figure 1).

within the perchlorate ions are normal.

The inner coordination sphere of the two independent Rh(III) ions has a nearly octahedral configuration with the trans bond angles ranging from 177.7 (2) to 179.1 (1)°. The small bite angles (between 75.9 (2) and 76.8 (2)°) are due to the small bite distances ranging from 2.508 (7) to 2.548 (7) Å. The Rh–N bond distances (2.021 (4)–2.077 (5) Å) are about the same as were found in *trans*-hydroxoaquabis(ethylenediamine)rhodium(III).[7]

The average C–C and C–N bond lengths within the bipyridine ligands compare well with those found in *trans*-Ru(bpy)$_2$(OH$_2$)(OH)$^{2+}$ [6] and in the free ligand.[8] The bipyridine rings, however, are twisted and bowed about the C5–C5′ axis. The angles between the least-squares planes through the atoms of the pyridine rings range from 16.5 to 32.0° for the four independent bipyridine ligands. This distortion of the bipyridine ligands is presumably due to the steric crowding experienced by the hydrogen atoms of the neighboring bipyridine ligands in the trans position. The contact distances between the α-hydrogen atoms (calculated from computed coordinates, C–H = 0.95 Å) vary between 2.14 and 2.27 Å (see Table III).

The O–O distances (2.565 (8) and 2.447 (6) Å) within the $H_5O_3^-$ bridging group suggest strong hydrogen bonds between the oxygen atoms. This together with the Rh–O bond distances (2.034 (5) and 2.038 (5) Å), which are about the same as was found in *trans*-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$ [7] for the Rh–O$_2$H$_3$ bond distance and significantly shorter than the Rh–OH$_2$ bond distance (2.090 (6) Å, also trans to a chloride ligand) in (NH$_4$)$_2$[RhCl$_5$(H$_2$O)],[9] suggests a $H_5O_3^-$ bridging group rather than two Rh–OH$_2$ bonds with a hydroxide ion (O3 in Figure 1) as counterion. The atomic coordinates of the hydrogen atoms of the $H_5O_3^-$ unit could not be obtained from the final difference Fourier. Furthermore, it may be noted that the O–O distances in the $H_5O_3^-$ group are about the same as in the $H_3O_2^-$ group in [*trans*-Co(en)$_2$(H$_3$O$_2$)](ClO$_4$)$_2$ (2.441 (2) Å),[10] [*cis*-Cr(bpy)$_2$(H$_3$O$_2$)]$_2$I$_4$·2H$_2$O (2.446 (5) Å),[10] [*trans*-Rh(en)$_2$(H$_3$O$_2$)](ClO$_4$)$_2$ (2.422 (3) Å),[7] [*trans*-Ru(bpy)$_2$(H$_3$O$_2$)](ClO$_4$)$_2$ (2.538 (6) Å).[6]

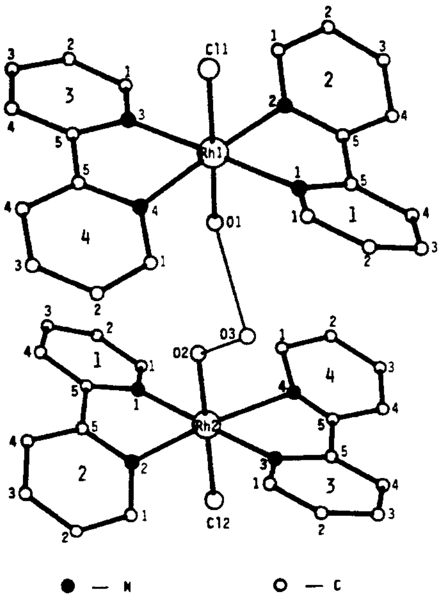

Figure 1. Numbering scheme of the atoms in the cation (see Table I).

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Table III. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses

Bond Distances within the Cation

Rh1–O1	2.034 (5)	Rh2–O2	2.038 (4)	Rh1–Cl1	2.291 (2)	Rh2–Cl2	2.272 (2)
Rh1–N11	2.056 (5)	Rh2–N21	2.061 (5)	O1–O3	2.447 (6)	O2–O3	2.565 (8)
Rh1–N12	2.021 (4)	Rh2–N22	2.026 (4)	N11–N12	2.508 (7)	N21–N22	2.530 (7)
Rh1–N13	2.077 (5)	Rh2–N23	2.051 (5)	N13–N14	2.548 (7)	N23–N24	2.545 (7)
Rh1–N14	2.034 (4)	Rh2–N24	2.047 (4)	O1–O2	3.601 (7)		

	Rh1				Rh2			
	ring 11	ring 12	ring 13	ring 14	ring 21	ring 22	ring 23	ring 24
N–C_1	1.338 (10)	1.315 (8)	1.338 (9)	1.320 (8)	1.328 (9)	1.315 (8)	1.343 (10)	1.324 (8)
N–C_5	1.348 (7)	1.364 (7)	1.354 (7)	1.360 (7)	1.369 (7)	1.360 (7)	1.362 (7)	1.370 (7)
C_1–C_2	1.406 (9)	1.401 (9)	1.411 (9)	1.397 (9)	1.396 (9)	1.396 (10)	1.412 (9)	1.393 (9)
C_2–C_3	1.389 (13)	1.375 (10)	1.383 (11)	1.383 (10)	1.386 (12)	1.375 (10)	1.375 (11)	1.378 (10)
C_3–C_4	1.388 (12)	1.374 (10)	1.370 (12)	1.372 (12)	1.376 (12)	1.379 (11)	1.399 (12)	1.371 (11)
C_4–C_5	1.407 (8)	1.384 (8)	1.416 (9)	1.393 (8)	1.393 (8)	1.391 (8)	1.397 (9)	1.390 (8)
C_5–C'_5	1.443 (9)		1.426 (9)		1.442 (9)		1.447 (10)	

Bond Distances between Hydrogen Atoms

H111–H141	2.20 (2)	H211–H241	2.16 (2)
H121–H131	2.14 (2)	H221–H231	2.27 (2)

Bond Angles within the Cation

Rh1		Rh2		Rh1		Rh2	
N1–Rh–N2	75.9 (2)	N1–Rh–N2	76.5 (2)	N2–Rh–Cl1	91.5 (2)	N2–Rh–Cl2	92.2 (2)
N3–Rh–N4	76.6 (2)	N3–Rh–N4	76.8 (2)	N3–Rh–Cl1	90.8 (2)	N3–Rh–Cl2	92.1 (2)
N1–Rh–N4	102.6 (2)	N1–Rh–N4	104.5 (2)	N4–Rh–Cl1	90.1 (2)	N4–Rh–Cl2	87.0 (2)
N2–Rh–N3	104.9 (2)	N2–Rh–N3	102.2 (2)	N1–Rh–N3	179.2 (2)	N1–Rh–N3	176.9 (2)
N1–Rh–O1	92.3 (2)	N1–Rh–O2	88.5 (2)	N2–Rh–N4	177.8 (2)	N2–Rh–N4	178.7 (2)
N2–Rh–O1	89.0 (2)	N2–Rh–O2	86.8 (2)	Cl1–Rh–O1	178.4 (1)	Cl2–Rh–O2	178.9 (1)
N3–Rh–O1	87.6 (2)	N3–Rh–O2	88.6 (2)	Rh–O1–O3	129.6 (3)	Rh–O2–O3	129.5 (2)
N4–Rh–O1	89.4 (2)	N4–Rh–O2	93.9 (2)	O1–O3–O2	91.8 (2)		
N1–Rh–Cl1	89.3 (2)	N1–Rh–Cl2	90.7 (2)				

	Rh1				Rh2			
	ring 11	ring 12	ring 13	ring 14	ring 21	ring 22	ring 23	ring 24
C_1–N–C_5	119.3 (5)	118.9 (5)	118.7 (5)	119.8 (5)	119.1 (5)	120.7 (5)	119.3 (5)	118.9 (5)
N–C_1–C_2	120.4 (7)	119.6 (6)	120.7 (6)	119.5 (6)	121.4 (6)	118.8 (6)	120.4 (6)	120.2 (6)
C_1–C_2–C_3	119.9 (8)	121.2 (6)	120.4 (7)	120.7 (7)	119.1 (8)	121.9 (7)	120.1 (8)	120.7 (7)
C_2–C_3–C_4	119.7 (6)	119.5 (6)	119.1 (6)	120.0 (7)	120.0 (6)	118.3 (6)	119.8 (6)	119.7 (6)
C_3–C_4–C_5	117.0 (7)	116.4 (6)	118.1 (6)	116.5 (6)	118.0 (6)	117.9 (6)	117.4 (6)	117.2 (6)
C_4–C_5–N	123.0 (6)	124.0 (5)	122.7 (6)	123.2 (6)	121.9 (6)	121.8 (6)	122.7 (7)	123.0 (6)
C'_5–C_5–N	113.1 (5)	113.1 (5)	114.3 (5)	114.5 (5)	114.0 (5)	113.0 (5)	113.6 (5)	113.7 (5)
C'_5–C_5–C_4	122.9 (5)	121.8 (5)	122.8 (5)	121.9 (6)	123.5 (5)	124.4 (5)	123.3 (5)	123.0 (6)

Angles between the Planes of the bpy Ligands

ring 11/ring 12	32.2	ring 21/ring 22	25.8
ring 13/ring 14	16.3	ring 23/ring 24	19.2

Infrared Spectra. There has been a long debate[1] about the usefulness of infrared spectra in identifying cis and trans isomers of $M(bpy)_2Cl_2^{n+}$ complexes. Furthermore, one also has to be aware of the influence of the crystalline environment and the counterion on the vibrational spectra of such cations, as has been shown for complexes of the type $M(bpy)_2Cl_2^+$ with M = Co(III), Cr(III).[11] Despite these restrictions, at least the study of the metal–halogen stretching vibrations can be helpful in elucidating the stereochemistry of these complexes. Bands that appear in the high-frequency region are not so metal sensitive, since they originate in the vibrations of the heterocyclic rings.

In the 4000–400-cm^{-1} region our spectra revealed only minor differences between related isomers, apart from the differences that we expected for the vibrations of water as well as ClO_4^- anion (see Figure A, supplementary material). The deviations that we want to mention refer to the bpy ring deformation and a C–H stretching mode. The ring deformation vibration, occurring at 401 cm^{-1} in free bpy, is typically raised by ca. 20–30 cm^{-1} on coordination of bpy to a metal. The trans complexes (see Figure 2) exhibit a single strong and sharp band at ca. 430 cm^{-1}, whereas the cis complexes have split bands at slightly lower frequencies. We also observed a displacement of a medium-intensity sharp band at 898 cm^{-1} for [*cis*-$Rh(bpy)_2Cl_2$]Cl·$2H_2O$ to 882 cm^{-1} for [*trans*-$Rh(bpy)_2Cl_2$]Cl accompanied by a weak band at 894 cm^{-1}. Corresponding bands of weak intensity for the *cis*- and *trans*-$Rh(bpy)_2(H_2O)Cl^{2+}$ complexes show a similar trend (898 cm^{-1} for cis, 889 cm^{-1} for trans). A strong band at 753 cm^{-1} and medium-intensity bands at 1039, 890, and 738 cm^{-1} have been assigned as H out-of-plane bending modes.[12] The complexes in Figure 2 have bands at very similar frequencies except for the mentioned differences in the 890-cm^{-1} region. Whether this is indicative of a particular interaction of the opposing protons in the trans complexes should be investigated further with other cis/trans isomers of bis(bipyridine) complexes.

In this respect it is important to note that Krause[13] reported the separation of cis and trans isomers of $[Ru(bpy)_2(py)_2](ClO_4)_2$ and $[Ru(bpy)_2Cl_2]$ by crystallization methods and characterized the products by infrared measurements in the 800–700-cm^{-1} region. He pointed out that only the trans isomer exhibits a weak band at 807 cm^{-1}. However, we found weak- to medium-intensity bands for all cis and trans isomers in Figure 2 within the 806–796-cm^{-1} range, although free bpy did not show bands in the 880–760-cm^{-1} range.

A region of particular interest is 400–200 cm^{-1}, where strong bands appear for the complexes that are absent in free bpy. Figure 2 illustrates the spectra recorded in this frequency range. The Rh–N and Rh–Cl skeletal modes were assigned for the cis com-

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plexes as in the literature[14] and are in good agreement with those for related complexes containing the RhN_4XY^{n+} configuration. Reduction of symmetry (from D_{2h} for trans to C_2 for cis, X = Y) leads to a loss of vibrational degeneracy and a splitting of the only infrared-active antisymmetric Rh–Cl stretching mode A_{2u} into the symmetric A_1 and the antisymmetric B_1 mode. Translabilization effects of coordinated chloride should shift the Rh–Cl vibration for the *trans*-dichloro complex to lower energy compared to that for the *cis*-dichloro species. However, the higher frequency of the 370-cm^{-1} band observed for the trans species compared to the 357- and 349-cm^{-1} bands for the cis species may indicate a strengthening of the Rh–Cl bond attributed to a π-overlap between the filled 3p orbitals of Cl and an extended π-system of the two nearly coplanar bpy ligands. Group frequency arguments suggest a single infrared-active Rh–N stretching vibration for the trans complex, and we assign the sharp band at 248 cm^{-1} of the *trans*-dichloro complex to the Rh–N vibration. It should degenerate into four vibrations for the cis complex, of which one is observed clearly at 269 cm^{-1} and three fall in the 290–280-cm^{-1} region.

In the case of a mixed trans complex with X $\neq$ Y the symmetry is also C_2. The two X–Rh–Y stretching modes are both of A_1 symmetry and can be divided into one in which the Rh–X stretch contributes mainly and one in which the Rh–Y stretch is more important. We assign the band at 368 cm^{-1} of the *trans*-chloro–aqua complex to the Rh–Cl vibration. From a comparison of the cis and trans structures, this band also shows a shift to higher energy as for the *trans*-dichloro complex.

By way of comparison we find a strengthening of the Rh–Cl bond when going from the cis to the trans complexes, but the opposite trend for the Rh–N bond. The broad band at 281 cm^{-1} for the *cis*-chloro–aqua complex can be located at 252 cm^{-1} for the trans complex.

Present uncertainties in the interpretation of the spectra in Figure 2 concern the bands in the 340–320-cm^{-1} region. It is also not possible to determine the symmetry species of the bonds observed in the infrared spectra since Raman data are still lacking.

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Supplementary Material Available: A table of anisotropic thermal parameters and complete infrared spectra of the species indicated in Figure 2 (6 pages); a table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

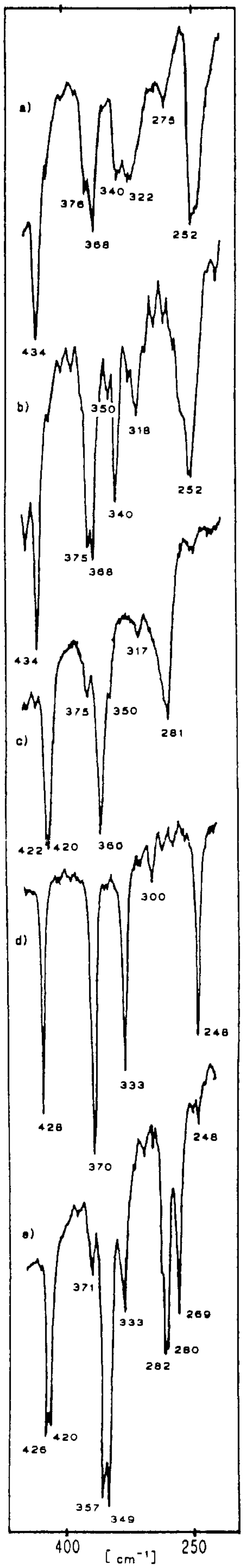

Figure 2. Far-infrared spectral bands of *cis*- and *trans*-$Rh(bpy)_2XY^{n+}$ complexes: (a) [*trans*-$Rh(bpy)_2Cl]_2(H_5O_3)(ClO_4)_3$; (b) [*trans*-$Rh(bpy)_2(H_2O)Cl](ClO_4)_2$; (c) [*cis*-$Rh(bpy)_2(H_2O)Cl](ClO_4)_2 \cdot H_2O$; (d) [*trans*-$Rh(bpy)_2Cl_2]Cl$; (e) [*cis*-$Rh(bpy)_2Cl_2]Cl \cdot 2H_2O$.

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Crystal and Molecular Structure of $[Cu(bcp)_2]BF_4 \cdot CH_3OH$ (bcp = 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)

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Complexes of the type $Cu(phen)_2^+$ and its variants, where phen denotes 1,10-phenanthroline, comprise a class of compounds in which there has been wide ranging interest, as is evident from reports on electronic spectra,[1–4] redox properties,[5–9] photochemistry

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